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CRYSTALLOGRAPHIC DATA FOR NICKEL AND COBALT BIURET COMPLEXES

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ABSTRACT. The crystallographic properties of nickel biuret and cobalt biuret complexes have been studied by means of X-ray diffraction data. The powder diffraction data showed that both the complexes belong to the monoclinic system. The cell dimensions for nickel biuret is a = 10.08 Å, b = 9.82 Å, c = 4.31 Å and $\beta = 101°18'$, while that of cobalt biuret is a = 6.06 Å, b = 11.05Å, c = 11.23 Å, and $\beta = 110°55'$. The systematic extinctions observed are consistent with the space group $P2_1/a$ with two molecules per unit cell for nickel biuret and $P2_1/c$ with two molecules per unit cell for cobalt biuret.

INTRODUCTION

Biuret is an organic compound derived from the products of the thermal decomposition of urea or urea nitrate. Because of its poisonous effect on some plants its presence in urea used as fertilizer is undesirable.

Schiff (1896) first reported the formation of chelate complexes of biuret with Cu and Ni salts. These complex formations subsequently serves a very useful method for the estimation of biuret in a very low concentration in urea. It has also been found that biuret can be estimated most satisfactorily by complex formation with Co-salts (Sanyal and Pal, 1964). The behaviour of chelating molecules and chelate complexes could ultimately be understood if the structure of the molecules are known in detail. Such question as the specificity (or the lack thereof) of a chelating molecule for inorganic ions, solubility, stability of the salts formed and many other physical properties could be easily answered only when the exact structures are known.

In order to explain such factors a preliminary investigation on the crystallographic properties of these complex salts have been undertaken.

EXPERIMENTAL

The nickel and cobalt biuret complex samples were prepared in accordance with the method followed by the previous workers in this laboratory (Sanyal and Pal, 1964). The samples were recrystallized from aqueous solution.

X-ray diffraction patterns of the above samples were obtained in Phillips X-ray diffractometer PW1050/51 with Geiger counter as detector. Filtered CuK_α radiation and cobalt radiation with iron filter was used. The interplanar

distances of the lattices were calculated from the measurement on X-ray diffraction patterns with maximum accuracy.

The phase identification was done by the usual method of Hanawalt *et al* (1938).

Interpretation of X-ray data :

The X-ray data are given in Tables II and IV. The powder pattern was indexed by Ito's method (Ito, 1950 ; Azaroff and Buerger, 1958). The interplanar spacing and corresponding Q values ($Q_{hkl} = 1/d^2_{hkl}$) are listed in Tables II and IV.

Nickel biuret :

The first three lines in the Tables II were first selected as Q_{100}, Q_{010} and Q_{001}. Then the higher orders of these lines i.e. Q_{200}, Q_{300} etc. were computed. An inspection of the observed Q's failed to show the computed values for these higher orders of Q i.e., Q_{200}, Q_{300} etc. So it was decided to select other possible values for the pinacoidal Q's. Accordingly, the first three lines were selected as Q_{200} Q_{020} and Q_{001}. It can be seen that the observed Q's are in quite agreement with the calculated Q values for other higher orders of reflection.

TABLE I

Selection of Q_{200}, Q_{020} and Q_{001}

Q_{hkl}	Computed	Observed	Error in Q_{hkl}
Q_{200}		.0359	
Q_{400}	.1438	.1449	+.0011/4=+.0002
Q_{600}	.3235	.3235	
Q_{020}		.0412	
Q_{040}	.1649	.1666	+.0017/4=+.0004
Q_{060}	.3711		
Q_{001}		.0541	
Q_{002}	.2163	.2200	+.0037/4=+.0009
Q_{003}	.4867		

From the table it can be seen that

$Q_{200} = .0359 + .0002 = .0361 = 2a^{*2}$

$Q_{020} = .0412 + .0004 = .0416 = 2b^{*2}$

$Q_{001} = .0541 + .0009 = .0550 = c^{*2}$

The dimensions of the reciprocal cell then becomes,

$a^* = .0948$ $\quad \alpha^* = 90°$

$b^* = .1019$ $\quad \beta^* = 78°41'$

$c^* = .2345$ $\quad \gamma^* = 90°$

Finally the other Q_{hkl} values were determined using the equation,

$$Q_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} = 2hka^*b^* \cos\gamma + 2klb^*c^* \cos\alpha^* + 2lhc^*a^* \cos\beta^* \qquad (1)$$

TABLE II

Final agreement of observed and computed Q_{hkl} 's for nickel biuret complex

Powder diagram line	dÅ	Q observed	Q computed	hkl.
1.	5.275	.0359	.0361	200
2.	4.925	.0412	.0416	020
3.	4.300	.0541	.0550	001
4.	3.910	.0654	.0654	011
5.	3.690	.0734	.0734	$20\bar{1}$
6.	3.427	.0851	.0812	111
7.	3.340	.0896	.0916	310
8.	3.230	.0959	.0966	021
9.	3.160	.1001	.1034	421
10.	3.122	.1026	.1026	130
11.	3.040	.1082	.1082	201
12.	3.000	.1111	.1124	121
13.	2.866	.1217	.1228	320
14.	2.820	.1257	.1297	230
15.	2.772	.1301	.1304	$40\bar{2}$
16.	2.730	.1342	.1310	$13\bar{2}$
17.	2.627	.1449	.1438	400
18.	2.522	.1572	.1548	410
19.	2.450	.1666	.1649	040
20.	2.400	.1736	.1748	330
21.	2.327	.1847	.1830	$12\bar{2}$
22.	2.242	.1989	.1980	321
23.	2.217	.2035	.2025	240
24.	2.132	.2200	.2163	002
25.	2.069	.2336	.2304	012
26.	2.045	.2391	.2372	141
27.	1.930	.2685	.2678	421
28.	1.824	.3006	.2936	212
29.	1.758	.3235	.3235	600
30.	1.681	.3539	.3522	312
31.	1.605	.3882	.3864	042

The direct cell dimensions are as follows :

$a = 10.68$ Å	$\alpha = 90°$
$b = 9.82$ Å	$\beta = 101°18'$
$c = 4.31$ Å	$\gamma = 90°$

The crystal therefore belongs to the monoclinic system. The indexed powder pattern showed the following systematic extinctions.

1. $0k0$ absent when k is odd.
2. $h00$ absent when h is odd.
3. $h0l$ absent when h is odd.

The space group indicated by these data is $P2_1/a - C^5_{2h}$.
The observed density of 2.653 gm cm^{-3} indicates 2 molecules per unit cell; calculated density = 2.54 gm cm^{-3}. The molecules must be centro-symmetrical with nickel atom at symmetry centres.

Cobalt biuret :

In this case first three lines in Table IV was selected as Q_{100}, Q_{020} and Q_{002}. It can be seen that the observed Q's are in quite agreement with the calculated Q values for other higher orders of reflection.

TABLE III

Selection of Q_{100}, Q_{020} and Q_{001}

Q_{hkl}	Computed	Observed	Error in Q_{hkl}
Q_{100}		.0312	
Q_{200}	.1248	.1245	$-.0003/4 = -.0000$
Q_{300}	.2809	.2805	$-.0004/9 = -.0000$
Q_{020}		.0329	
Q_{040}	.1317	.1322	$+.0005/4 = +.0001$
Q_{060}	.2964	.2980	$+.0016/9 = +.0001$
Q_{002}		.0365	
Q_{004}	.1459	.1457	$-.0002/4 = -.0000$
Q_{006}	.3284	.3280	$-.0004/9 = -.0000$

From the table it can be seen that,

$$Q_{100} = .0312 + .0000 = .0312$$
$$Q_{020} = .0329 + .0001 = .0330$$
$$Q_{002} = .0364 + .0000 = .0365$$

TABLE IV

Final agreement of observed and computed Q_{hkl}'s for cobalt biuret complex

Powder diagram lines	dÅ	Q observed	Q calculated	hkl.
1.	5.660	.0312	.0312	100
2.	5.510	.0329	.0330	020
3.	5.235	.0364	.0364	002
4.	5.036	.0394	.0394	110
5.	4.990	.0401	.0400	$20\bar{2}$
6.	4.890	.0419	.0419	021
7.	4.820	.0430	.0430	$10\bar{2}$
8.	4.780	.0437	.0444	$13\bar{2}$
9.	4.490	.0496	.0447	012
10.	4.420	.0511	.0481	$21\bar{2}$
11.	4.160	.0577	.0606	111
12.	3.995	.0627	.0642	120
13.	3.645	.0753	.0728	222
14.	3.310	.0913	.0913	102
15.	3.260	.0941	.0903	013
16.	3.120	.1027	.1000	112
17.	3.060	.1068	.1050	130
18.	3.020	.1096	.1103	032
19.	2.834	.1245	.1248	200
20.	2.785	.1289	.1262	131
21.	2.750	.1322	.1320	040
22.	2.680	.1392	.1403	041
23.	2.620	.1457	.1459	004
24.	2.245	.1984	.1986	230
25.	2.214	.2040	.2096	202
26.	2.114	.2238	.2252	104
27.	1.888	.2805	.2808	300
28.	1.810	.3052	.3013	035
29.	1.796	.3100	.3122	223
30.	1.772	.3185	.3138	320
31.	1.745	.3284	.3284	006

The dimensions of the reciprocal cell thus becomes,

$a^* = .1766$	$\alpha^* = 90°$
$b^* = .0905$	$\beta^* = 69°4'$
$c^* = .0954$	$\gamma^* = 90°$

Finally the other Q_{hkl} values were determined using the equation (1).
The direct cell dimensions are as follows:

$a = 6.06$ Å	$\alpha = 90°$
$b = 11.05$ Å	$\beta = 110°55'$
$c = 11.23$ Å	$\gamma = 90°$

In case of cobalt biuret complex the crystal belongs to the monoclinic system. The indexed powder pattern showed the following extinctions.

1. *oko* absent when k is odd.
2. *ool* absent when l is odd.
3. *hol* absent when l is odd.

The space group indicated by these data is $P2_1/c-C^5_{2h}$.
The observed density of 2.542 gm cm^{-3} indicates two molecules per unit cell; calculated density = 2.436 gm cm^{-3}.

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